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VOLUME XII OCTOBER 8, 1923 NUMBER 21

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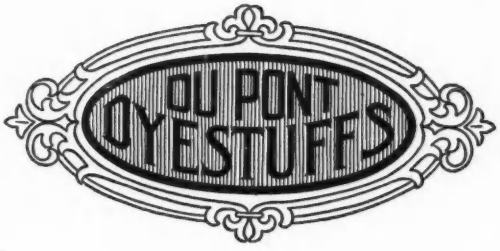

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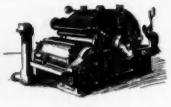

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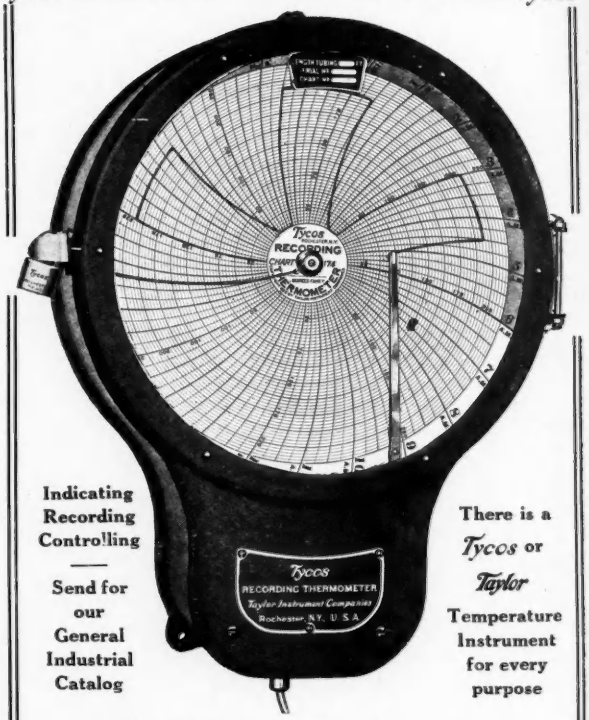

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VOLUME XII NEW YORK, OCTOBER 8, 1923 NUMBER 21

Influence of Metallic Hydroxides on Fastness to Light of Indigo

By DR. R. HALLER

(*Textilberichte*, 1923, 229-230)

Translated for The Reporter by ISMAR GINSBERG, B.Sc., Chem. Eng.

VARIOUS experiments and investigations have been made in the past in the attempt to improve the fastness of cotton dyestuffs to light. In these experiments the colored fabrics were impregnated with 10 per cent solutions of almost all the common salts that are purchasable on the market, and then exposed to the action of direct sunlight. It was concluded therefrom that none of the impregnations had any effect on the fastness to light of the unstable basic dyestuffs which were used in coloring the fabrics. However, in the case of certain substantive dyestuffs that are used in dyeing cotton fabrics and that yield shades which are not fast to light, the fastness to light was materially improved by the action of certain salts, such as sodium thiosulphate, copper sulphate, nickel sulphate and cobalt sulphate. When woolen samples which had been impregnated with the same salts mentioned above were subjected to the action of light, it was characteristically found that these salts possessed no power in increasing the resistance of the dyed fabrics to light. It was remarked, on the other hand, that the fastness to light of the dyestuffs Malachite Green, Victoria Blue and Methyl Violet was improved when the dyed samples of cloth were impregnated with a solution of potassium ferrocyanide. From certain experiments which were carried out by Krais (see Zeitschrift fuer Farben und Textilchemie, 1902, 22), it was concluded that this action of potassium ferrocyanide was not secured by the direct influence of the salt on the dyestuffs, but through a secondary reaction, as it may be called, with the Berlin Blue that was formed from the potassium ferrocyanide.

The author himself conducted a series of experiments on this problem some time ago. Fabrics were chosen which were first treated in a bath of potassium ferrocyanide and then printed with the aid of dyestuffs such as Ethyl Green. Metallic salts were added to the dyestuff paste that was used in printing the fabrics. These salts were so chosen that they possessed the property of forming corresponding ferrocyanides with the potassium ferrocyanide present in the goods. Particularly in the case where copper salts were used it was observed that they exerted a very favorable influence on Ethyl Green, which under ordinary conditions gives a coloration which is extraordinarily sensitive to the action of light. Under present conditions, wherein particular attention is paid to the production of goods of the highest possible quality, the fact that this treatment also has a slight effect in enhancing the strength of the fabric and of the color as well represents an additional advantage.

Fastness of Indigo to Light

Indigo is supposedly a dyestuff which is extremely fast to light, but it possesses other properties which might well be as advantageous as the former. The author refers only to its insufficient fastness to rubbing. But then again, neither is the fastness to light so absolute that it leaves no doubt in mind as to how the dyestuff will behave when exposed to strong light. It is a fact that when a piece of goods which has been dyed with indigo has been exposed to the direct rays of the sun under conditions of bright and strong sunlight, this exposure is sufficient to completely bleach out the average indigo color. The great popularity which the dyestuff indigo possesses at the present time, and which seems to be ever on the increase, is due not to its great fastness to light but to other advantageous properties with which it is endowed. Thus, for example, it is known that indigo is mordanted on textile fabrics with great ease, much more readily than the majority of dyestuffs; and, furthermore, it can be subjected to the action of a resist just as easily. Then, again, in contradistinction to a great many other dyestuffs which perhaps may be designated as just as fast

to light as indigo, it always keeps its clear blue hue when subjected to washing and light, except under the extraordinary conditions mentioned above. However, it is evident that the dyestuff would become of even greater value if success would crown the attempts to improve its rather inconvenient and unsatisfactory properties in one way or another.

Metal Salts and Their Action on Indigo

As a corollary to the investigations of Krais, as well as to certain experiments and studies made by the author himself, an investigation was started to determine whether or not it was possible to effect any material change in the fastness of indigo to light by the action of metallic oxides so as to render fabrics dyed with indigo more resistant to light. To accomplish this, fabrics were printed with indigo pastes of the average quality and then treated with solutions of metallic salts in various concentrations. The metallic hydroxides were then precipitated on the fabrics by passing them through a dilute, warm solution of lye. The fabrics were then well washed out and finally dried. The fabrics obtained in this manner were then subjected to the light of the sun in such a manner that only one-half of each sample, covered with a glass plate, was exposed to the sun's rays. The experiment was made during the months of July and August.

If the resistance of the dyed fabric to light is changed in any respect by this treatment it will be manifested in a difference in the intensity of the color in that part of the fabric which had been treated with the metallic salts in comparison with that part which had not been treated in this fashion. In other words, a control sample was used in each case so that any difference which gradually evolved during the course of the exposure of the dyed fabrics to the direct rays of the sun might be detected and measured. The fact is that it did not take very prolonged exposure of the dyed fabrics to the sun's rays to show that the treatment of the dyed fabric with certain metallic salts was really of important benefit in increasing the resistance of the dyestuff to light.

The Indigo Blue fabrics were printed with a printing paste which had the following composition: 100 grams of neutral British gum-starch thickening and 10 cubic centimeters of a solution of metallic salt in water containing a quantity of salt equivalent to the molecular weight of the same dissolved in a liter of water. After the fabrics were dried they were passed in a warm solution of caustic soda containing 10 grams of 38-degree BeNaCH in 1 liter of water. The fabrics were then washed, and finally dried.

Experimental Results

The results that were obtained after two months' exposure to light are given in the following tabulation:

1. Magnesium Chloride—Printed and unprinted parts bleached out in equal degrees.
2. Aluminum Sulphate—Printed and unprinted parts bleached out in equal degrees.
3. Chrome Alum — Printed and unprinted parts bleached out in equal degrees.
4. Iron Chloride—Printed parts entirely unchanged; unprinted parts completely bleached.
5. Titanium Chloride—Acts on the printed portions of the fabric as well as on the unprinted portions, which are both bleached.
6. Nickel Sulphate—Those parts of the fabric which were printed are protected against the light to some extent.
7. Cobalt Nitrate—The printed parts of the fabric are not so strongly bleached as the unprinted parts.
8. Manganese Chloride—Printed parts of the fabric are unchanged; unprinted parts are bleached.
9. Zinc Sulphate—Printed parts of the fabric are not much less bleached than the unprinted parts.
10. Corrosive Sublimate—There is only a very slight difference between the printed and unprinted parts of the fabric.
11. Lead Acetate—Almost no difference between the printed and unprinted parts of the fabric.
12. Bismuth Nitrate—Both the printed and unprinted parts of the fabric are bleached in equal degrees.
13. Copper Sulphate—The printed parts of the fabric remain almost unchanged.
14. Cadmium Sulphate—Exerts a slight protective action on the printed parts of the fabric.
15. Stannous Chloride—Exerts a slight protective action on the printed parts of the fabric.
16. Gold Chloride—This salt has no action on the fabric.
17. Chlorplatinic Acid—No action on the fabric.
18. Palladium Chloride—Exerts a slight protective action on the printed parts of the fabric.
19. Silver Nitrate—Almost no change in the printed parts.

Discussion of Results

From this tabulation it is clearly seen that there are certain metallic salts which possess an actual, inherent, protective action on indigo-dyed fabrics in aiding them to resist the influence of light. The most effective seem to be the manganese salts; then come the salts of the metals of the iron group, with those of iron the most conspicuous. The salts of copper also possess an extraordinary protective action on the indigo-dyed fabrics. In this connection it will be remembered that the copper salts also seem to possess the power of protecting fabrics which are dyed with other coloring matters against the action of light. In the case of silver, whose salts also possess remarkable protective power, it is unfortunate that it is impractical to use the salts in commercial work for self-evident reasons.

For the sake of making the investigation complete, and in order to substantiate certain conclusions that the author reached in some earlier investigations that he made on this problem, he tested out the protective power of the ferrocyanides and the ferricyanides of several metals; as, for example, silver, zinc and copper.

Solutions of these salts in molecular proportions were prepared and the fabrics were first printed with indigo paste containing salts of these metals in the same manner as described in the first series of tests. Then the fabrics were dried and passed into solutions of ferrocyanide and ferricyanide. After the test samples had been exposed to the light for a period of two months—in this case, as well, the exposure was made during the two summer months July and August—it was found that this treatment did not yield any satisfactory results. The printed parts of the fabric in which the silver salt was used became olive in color. The zinc salt showed no protective action at all, while the copper salt seemed to have some protective action, for the printed parts of the fabric were much darker in color after exposure than the unprinted parts. On the other hand, the color tone was completely changed, due to the reddish-brown copper ferrocyanide which was deposited on the fabric.

The general conclusion that may be drawn from this investigation is that it is within the realms of possibility to protect indigo-dyed fabrics against the bleaching action of direct sunlight. The process can be worked out on a practical scale. Of all the metallic salts that were tested out in this research, the salts of iron appeared to be best suited for use in the process from a practical and economic standpoint.

A Method of Determining the Detergent Action of Soaps*

By J. W. McBAIN, R. S. HARBORNE, and A. MILLICENT KING

Department of Physical Chemistry, University of Bristol

IN spite of the many investigations on the subject of detergent action (*cf.* McBain, Third Colloid Report of the Brit. Assn. for Adv. of Sci., 1920, p. 24), there is still no recognized standard in terms of which the washing power of soaps can be expressed. This communication describes quantitative measurements of detergent action upon one substance; namely, carbon black.

Striking, although only qualitative, experiments describing the action of solutions of a "medicinal soap" in suspending lampblack were published by Spring (Kolloid-Zeits., 1909, 4, 164; also Rec. Trav. Chim. 28, 120). He found an optimum effect in 1 per cent solution, and even in dry methyl and ethyl alcohols there was an optimum concentration, although in very much more dilute solution. He also found that dilute aqueous soap solutions had the power of carrying a certain portion of the lampblack through a filter paper, although this did not occur when using alcohol.

Spring concluded that a sorption compound was formed between the lampblack and the soap, or rather (upon rather doubtful evidence) between lampblack and somewhat acid soap. The suspended lampblack passed through filter paper without blackening it, although, in the absence of soap, none passed through, and the black clung tenaciously to the paper. Spring's conception of detergent action is, therefore, represented by an equation of the form:

$$\text{Fabric.dirt} + \text{soap} = \text{fabric} + \text{dirt.soap}$$

McBain (*loc. cit.*) proposed the more logical alternative of double decomposition, namely:

$$\text{Fabric.dirt} + \text{soap} = \text{fabric.dirt} + \text{soap.dirt}$$

for which there is a good deal of evidence.

In Spring's experiments with lampblack and in ours with carbon black only a portion of the carbon, that stably suspended, is carried through the filter paper. We utilize this fact and simply determine the amount of carbon black carried through. The "carbon number" of a soap solution is the number of grams of carbon carried through by one kilogram of soap solution under standard conditions.

Preliminary Experiments by R. A. W. Bond

Much time was spent by R. A. W. Bond in studying various samples of lampblack and carbon black. That which gave the largest effect was "Auk" carbon black, a 15-pound samples of which was supplied through the kindness of Messrs. Chance and Hunt, of London. Their "Kalista" carbon black was only slightly less effective

*A paper prepared for the Society of Chemical Industry, and published in the Journal of the Society.

Extraction of the carbon black with ether in a Soxhlet apparatus was detrimental, owing to the agglomeration of the carbon; hence, in all further work untreated original carbon black was employed.

Twenty cubic centimeters of soap solution carried through most carbon when shaken with 1 g. of carbon black, this amount being more effective than either 2 or 0.5 g.; thus in experiments with No. 5 Whatman filter papers and 0.1*N*w potassium myristate the carbon numbers found were 0.56, 0.33 and 0.11, respectively. No explanation is afforded.

A large number of filter papers were tested and No. 31 Whatman filter paper was finally adopted as being most porous and yet fairly uniform. For the gravimetric analysis of the filtrate the only satisfactory paper was No. 590 Schleicher and Schull filter paper.

Time of exposure of the lampblack to the soap was varied from one day to one month without noticeable effect. Increase of temperature greatly diminished the carbon number. It was found in accordance with expectation that there was an optimum concentration of soap solution.

Experimental

Materials.—Only soaps prepared from pure fatty acids were used; the potassium oleate was prepared by Kahlbaum and contained three equivalents per cent excess acid. Other soap solutions were prepared with the precautions described by Bunbury and Martin (Chem. Soc. Trans., 1914, 105, 417), from pure fatty acids supplied by Kahlbaum but using Jena glass vessels with well vaselined glass stoppers. The importance of the last precaution, which is invariably adopted in this laboratory, is strikingly illustrated by the following Table I:

Table I

Acidities of potassium oleate solutions in equivalents of free acid to 100 equivalents of soap.

Description of Solutions	Stopper Employed	Acidity When Fresh	Acidity Next Day
Soap dissolved in 2 parts alcohol + 1 part water:			
Sample I	Unvaselined glass	2.87	4.11
Sample II	Vaselined glass	2.89	2.93
0.05 *N*w aqueous sol. + 2 parts alcohol.....	Well vaselined cork...	7.67	16.36
0.496 *N*w aqueous sol. + 2 parts alcohol.....	Well vaselined glass...	3.27	3.34

Increase in acidity is due chiefly to entrance of carbon dioxide, but partly to oxidation. Distilled water and alcohol were always boiled out in a pyrex flask. The acidimetric standard was benzoic acid supplied by the Bureau of Standards, Washington, and constant-boiling hydrochloric acid prepared by the method of Hulett and Bonner. The great importance of exact neutrality is shown by the sequel. As far as possible dilute solutions were prepared by direct dilution of more concentrated stock solution, but a large number of independent solutions were also made up.

Procedure.—In determining the amount of carbon carried through a filter paper by soap solution the following standard method was adhered to: One gram of "Auk" carbon black, weighed within 1 per cent, was placed in a large test tube with 20 c.c. of the soap solution, shaken thoroughly, and allowed to stand for twenty-three hours in a thermostat at the experimental temperature, shaken again and allowed to stand a further hour before being poured upon an 11.3-cm. No. 31 Whatman filter paper. The filtration was also carried out in the same thermostat (a water-jacketed copper chest kept within 0.5 degree) and allowed to stand until approximately 10 c.c. of filtrate had collected. The filtrates were then analyzed either by the gravimetric or, in all later work, the colorimetric method. The data given in the present paper enable absolute results to be readily obtained in other laboratories by simple comparison with ours.

Gravimetric Method of Analysis.—The carbon in the filtrate had to be isolated and weighed on a filter paper. A 5.5-cm. 590 Schleicher and Schull filter paper, which had previously been extracted with alcohol in a Soxhlet extractor, was dried at 110 deg. Cent. in an electric oven for forty-five minutes. It was then transferred quickly to a small weighing bottle fitted with an air-tight stopper. The filter paper was weighed by difference and the drying repeated until the weight (about 0.12 g.) remained constant to 0.1 mg. It was then necessary to obtain on this dried analysis filter paper the whole of the carbon in the filtrate. Two methods were adopted, depending on whether the concentration of the soap was greater than or less than 0.3*N*. In the latter case, the carbon suspension (i. e., the filtrate) was decomposed by the addition of about 20 c.c. of alcohol and filtered through the analysis paper, the whole of the carbon being retained without difficulty. The carbon was then thoroughly washed free from soap with hot alcohol. When the concentration of the soap solution was above 0.3*N*, it was found that so much alcohol was required to break the suspension and dissolve the soap that the time taken to filter this large bulk of liquid was too long for the first method to be employed.

In the second method, the suspension was decomposed by the addition of a few cubic centimeters of dilute sulphuric acid (approximately 0.5*N*). The water was then decanted, through the analysis filter paper, from the fatty acid precipitate formed, and the latter melted by warming to about 60 deg. Cent., and poured onto the filter paper. The tube and filter paper were then washed free from fatty acid by means of hot alcohol, the carbon being retained on the filter paper. The alcoholic washings were tested for fatty acid by dilution with cold water, a white ring of myristic acid precipitate being formed if not free from fatty acid. This washing operation had to be carried out with great thoroughness, otherwise misleading high results were obtained.

The filter paper and carbon thus obtained were then dried in the electric oven and weighed under conditions as far as possible identical with the previous drying and weighing; i. e., dried at 110 degrees for forty-five minutes and weighed in an air-tight weighing bottle. The increase in weight gives the weight of carbon in a known weight of filtrate, which is then expressed in "carbon numbers," grams of carbon per 1 kg. of soap solution.

This method of analysis is restricted in use, although essential for obtaining an absolute standard for all subsequent work. In the first place, the limit of weighing on an ordinary chemical balance gives a possible error in the carbon number of about 10 per cent for a 0.1*N* solution when only 10 g. of filtrate is taken. If more than 10 g. of filtrate is taken the bulk of the liquid becomes great, thus making the process of filtering off the carbon from the decomposed filtrate very long and tedious. Moreover, as the amount of carbon on the analysis filter paper increases beyond about 10 mg., the time taken to wash free from acid or soap is so long that the probability of error from incomplete washing overwhelms the advantage of having a comparatively large amount of carbon on the filter paper.

It is therefore seen that the gravimetric method may only be used with advantage with such concentrations of soap solutions as give a carbon number of about 0.5 to 1.0, unless a micro-balance accurate to within 0.01 mg. is used.

Colorimetric Method of Analysis.—In this method the filtrates (about 10 g. in every case) were diluted to known volume by the addition of a large excess of alcohol. For the sake of convenience, these diluted filtrates are termed "test filtrates." A convenient concentration was obtained by weighing out accurately about 1 g. of filtrate and diluting to 100 c.c. with alcohol, the solution being well shaken and allowed to stand for a few minutes before being analyzed in order that the alcohol might dissolve the soap. The length of column required to give the same transmission of light as a column of standard test filtrate was then ascertained by means of a colorimeter. According to Beer's law, the amounts of carbon in the two test filtrates are inversely proportional to the length of the columns giving the same transmission of light. Thus the concentration of the filtrates can quickly be compared with that of the standard filtrates. A Donnan colorimeter was used, but less accurate comparisons could be made by eye.

The carbon number of the filtrate is given by the formula:

$$C = \frac{ls\ ws}{l\ w} \cdot Cs = 0.54\ \frac{ls\ ws}{l\ w}$$

where ls and l are the lengths of the columns of standard liquid and filtrate respectively and ws and w are the weights of standard and of filtrate which have been diluted to 100 c.c. with alcohol.

The filtrate from 0.125*N*w potassium myristate was arbitrarily chosen for the standard test filtrates because the value of the carbon number had been carefully established for this case by the gravimetric method of analysis as 0.54+ or —0.01.

The final step toward simplifying the manipulation and rendering it possible for other laboratories to obtain results in our units was made by replacing the standard filtrate by a dye solution of similar color prepared from pure dyes obtained from British Drug Houses, Ltd. The specification of this standard was: 50 c.c. of nigrosine solution of concentration 0.056 g. per liter, 20 c.c. of Bismarck Brown solution of concentration 0.0858 g. per liter, 100 c.c. of distilled water. This dye solution was found equivalent in light transmission to a test filtrate of carbon number 1.19. The carbon number value of 1.19 was the absolute value obtained by comparing the dye standard in the colorimeter with test filtrates prepared from filtrates which had been analyzed gravimetrically. This dye standard, which is quickly prepared and easily reproducible, possesses many advantages as a standard over any filtrate, which is not only subject to a greater experimental error in preparation but also liable to error due to occasional non-uniformity of the filter papers.

Hence, to obtain the carbon number of any commercial soap, using a sample of our carbon black, it is only necessary to compare the filtrate (after diluting w grams to 100 c.c. with alcohol) with the standard dye solution and apply the formula:

$$C = 1.19\ \frac{ls}{lw}$$

We are prepared to supply small samples of our carbon black for purposes of standardizing the stock used by other investigators. The same result can be obtained quite independently by carefully preparing any of the soap solutions whose carbon numbers are properly recorded in this paper and standardizing the carbon black or other carbon therewith; it is only necessary to determine with that soap solution the ration between the depth of color of the filtrate obtained and the color here recorded to have a constant factor which will convert all experimental results, using commercial soaps, with any definite kind of carbon or lampblack, into the standard units of carbon number.

Experimental Results

Concentrations of soap are expressed in per cent.—i. e., grams of soap in 100 g. of solution—as well as in weight normality (*N*w)—that is, gram-equivalents of soap in 1 kg. of water.

Table II contains the data for various concentrations for pure potassium myristate at temperatures between

12 and 15 deg. Cent. Each value is the mean of a large number of determinations.

Tables III and IV exhibit the important influence of very slight additions of either free alkali or free fatty acid. Table V shows the effect of change of temperature. Table VI gives the results for various concentrations of potassium oleate, and here the filter paper was folded by gentle pressure between finger and thumb, since it had been found by Messrs. Allnutt that increased pressure may cause slower filtration and give inconsistent results (Chem. & Ind., 1923, 565).

TABLE II (see Graph I)

Variation of carbon number with concentration of solutions of neutral potassium myristate

Soap %	Soap Nw	Mean Carbon Numbers Gravimetric (12°-15°)	Colorimetric (12°-15°)
0.268	0.01		0.03
0.662	0.025		0.10
1.32	0.05	0.17	0.21
1.96	0.075	(0.47)	0.32
2.59	0.10	0.49	0.41
3.22	0.125	0.54 + or − 0.01	0.54*
3.84	0.150		1.28
4.45	0.175		2.18
5.06	0.20		0.40
6.24	0.25		0.35
7.40	0.30	0.29	0.30
9.63	0.40		0.22
13.8	0.60		0.025
18.0	0.80		0.01

*Indicates standard upon which all colorimetric readings are based.

TABLE III (see Graph II, right-hand portion)

Carbon numbers of potassium myristate + excess of potassium hydroxide

Soap %	Soap Nw	Excess of KOH Nw	Equivalents %	Temp. °C.	Carbon No.
3.22	0.125	0.000	0	15	0.54
"	"	0.00125	1	16	1.27
"	"	0.00625	5	16	2.06
"	"	0.0125	10	16	3.98
"	"	0.0218	15	14	2.83
"	"	0.0250	20	16	3.02
"	"	0.0375	30	14	4.09
"	"	0.0500	40	13.5	5.60
"	"	0.0625	50	13.5	10.0
"	"	0.0750	60	14	3.52
"	"	0.0875	70	14	4.22
"	"	0.125	100	13	3.58
"	"	0.250	200	13	1.23
"	"	0.375	300	13	0.83
"	"	0.625	500	13	0.27
4.45	0.175	0.00875	5	11.5	0.65
"	"	0.0175	10	11.5	2.60
"	"	0.0262	15	13	7.38
"	"	0.0525	30	11.9	6.7
"	"	0.0875	50	11.5	6.25
"	"	0.776	100	11.5	3.16

TABLE IV (see Graph II, left-hand portion)

Carbon numbers of 0.125*Nw* (= 3.22%) *potassium myristate solution + excess of myristic acid*

% (of concn. of soap) Excess Myristic Acid	Mean Carbon No.	Temp. °C.
0	0.54	15
1	1.6	12
5	1.9	12
10	2.0	11
20	1.21	11
50	0.58	11

TABLE V

Variation of carbon number of pure neutral 0.1*Nw* (= 2.59%) *potassium myristate with temperature*

Temperature	11.5°	15°	25°	60°
Carbon no.	0.51	0.41	0.22	0.15

TABLE VI (see Graph III)

Variation of carbon number of solutions of potassium oleate with concentration

Soap %	Soap Nw	Independent Results Temp. °C.	Independent Results Carbon No.	Curve I* Temp. °C.	Curve I* Carbon No.	Curve II Temp. °C.	Curve II Carbon No.
19.8	0.77	12.0	1.29				
13.9	0.503					20.5	0.12
12.9	0.495	12.1	0.10	13.9	0.17	17.5	0.11
12.6	0.450			13.9	0.17		
11.4	0.40			13.4	0.31	17.6	0.13
10.9	0.38	12.5	0.31				
10.1	0.35			13.4	0.36	17.4	0.21
9.44	0.325			13.3	0.45	17.4	1.03
8.77	0.30	14.75	1.09	13.6	0.39	17.5	2.16
		13.10	2.14			19.5	2.27
		19.5	2.27				
8.50	0.29			13.7	0.51		
8.40	0.826	14.75	1.65				
		14.50	3.20				
7.96	0.27			13.7	0.57	17.6	1.53
7.50	0.253	12.8	1.05				
7.42	0.25	11.5	1.17	13.5	0.47	17.8	1.33
6.73	0.225	12.50	2.24			18.6	1.21
6.02	0.20	12.55	3.53	13.6	0.77	18.6	0.82
		13.45	2.42			19.8	1.60
		14.5	1.78			20.7	0.87
		19.4	1.96				
5.60	0.185			13.9	1.14		
5.30	0.175			14.2	1.44		
4.97	0.163			15.3	1.15		
5.07	0.167	12.4	2.33				
5.26	0.173			15.2	1.23		
4.59	0.15			14.1	0.90	19.5	0.63
3.85	0.125	11.5	0.71	14.2	0.83		
		14.5	1.35				
3.11	0.10	17.5	0.86	14.5	0.49	17.5	0.72
2.29	0.073			14.7	0.44		
1.58	0.05	13.7	0.56	14.6	0.33	19.8	0.84
0.984	0.031	21.0	0.38				
3.11	0.10	17.5	0.52			19.4	1.17

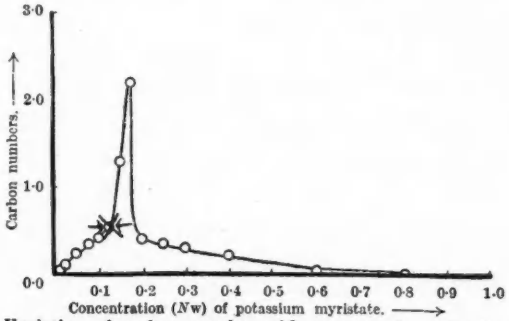
*In the series of experiments in Curve I unsatisfactory illumination was employed in the colorimeter. Each number in Table VI is the mean of three or four results.

Discussion of Results

It is seen from the tables and graphs that the results are dependent upon concentration, temperature, acidity and alkalinity.

There is a surprisingly sharp maximum carbon number at a particular concentration of soap. In the case of potassium myristate this occurs at a concentration of $0.175Nw$ (= 4.45 per cent), which is a hundred times more effective than either a very dilute or concentrated soap solution. In the case of potassium oleate the existence of a similar maximum is equally obvious, and it lies in only slightly higher concentration, although here the effects are obscured by the great sensitiveness of oleate solutions to other external factors. It is well authenticated that there is an optimum concentration for the use of any commercial soap as a detergent. In applying this to practical washing operations it may easily be advisable to use a strong solution and to pass through the optimum concentration in the rinsing process.

The actual detergent powers of the two very different soaps, myristate and oleate, are unexpectedly similar, although the first is derived from a saturated fatty acid containing only fourteen carbon atoms, whereas the other is unsaturated, containing eighteen carbon atoms, and the oleates are regarded as soaps *par excellence*. where is no other property of soap solutions which is known to be at an absolute maximum at these concentrations, although



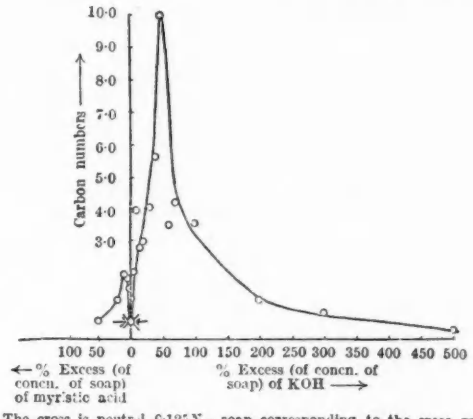
Variation of carbon number with concentration of solutions of neutral potassium myristate.

Graph I.

the turbidity of such colloidal systems as soap and cellulose acetate may pass through an ill-defined maximum at similar concentrations. There is likewise no constituent of soap solutions, except possibly the hydroxyl ion, which passes through a maximum of concentration in this reyion.

Very slight excess of either acid or alkali increases the detergent action manifold, although further excess causes it again to disappear. This is probably the chief cause in the fluctuations in the results with the oleate, which so readily oxidizes in the air with corresponding change in alkalinity. In the case of $0.125Nw$ (= 3.22 per cent) potassium myristate, addition of 50 equivalents per cent of alkali (= only $0.0625NwKOH$) increases the detergent action nineteen-fold.

Temperature exhibits an important effect, especially at lower temperatures, where the carbon number very rapidly increases, being doubled for a change of 10 degrees. The effect is very much less at higher tempera-



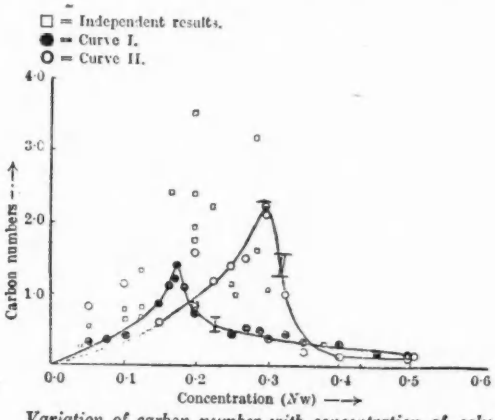
The cross is neutral $0.125N_w$ soap corresponding to the cross on Graph I.

Variation of carbon number of 0·125 N_w potassium myristate solution with excess of myristic acid and KOH.

Graph II.

tures. It is known that the amount of colloidal soap behaves in a somewhat similar fashion.

In Graph III for solutions of potassium oleate, the two series of points connected by a continuous line represent solutions which were prepared by dilution of one sample of the most concentrated solution; the other points represent solutions made up quite independently. Miss Laing has found that solutions of sodium oleate require at least a day to attain internal equilibrium at room temperature, and it is possible that even the hydrolysis alters. A direct test should be made upon the effect of time upon the de-



Variation of carbon number with concentration of solutions of potassium oleate.

Graph III.

tergent action of oleate solutions. Some of the erratic results were undoubtedly due to faulty filter paper, since occasionally some of the carbon coming through with the filtrate settled immediately to the bottom of the test tube

(*Continued on page* 731)

AMERICAN
DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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THE REPORTER AND THE TEXTILE EXPOSITION

THE next issue of The REPORTER, published October 22, will be in the nature of a special issue to be used in conjunction with the Textile Exposition to be held in Boston the week of October 29. In addition to containing several articles of more than ordinary interest, it will have what is with us, at least, a novel feature, in that it will include several sample cards showing dyeings on both piece goods and yarn as prepared by some of the leading dyestuff manufacturers.

At the Textile Exposition The REPORTER will be represented in Booth No. 600, where we shall hope to have the pleasure of welcoming all of our subscribers and friends who visit the Exposition. Incidentally, this booth will serve as headquarters for the American Association of Textile Chemists and Colorists, and it is particularly requested that all visiting members of this organization leave their names and Boston addresses at the booth in order that their local whereabouts may be known.

WHY IS THE CHEMICAL EXPOSITION?

THE Ninth National Exposition of the Chemical Industries, recently held in this city, was useful, if for nothing else, in enabling those interested in chemical developments in this country to estimate the value of these exhibitions.

They are prepared at considerable expense on the part of the exhibitors, but there is a very general dubiety as to their value as investments.

This feeling was undoubtedly at the bottom of the determination to hold the Exhibition every other year, and there would seem to be little doubt, in view of what the exposition has come to be, that this decision was a wise one.

At the same time it is not improper to ask what the purpose of these elaborate assemblings of chemical apparatus and records of accomplishment may be, and what object they should most effectively serve.

Are they to be looked upon simply as bazaars or fairs at which sales are to be made, and the cost of which is expected to be written off in the business actually done; or are they to serve the purpose of informing the public, periodically, of the progress made in the chemical industry; of new discoveries made; of new dyes developed; and of new claims on the confidence of the people of this country, without which the industry cannot hope to secure that legislative support which is essential to its permanent establishment and continuity.

The recent exhibition was almost exclusively one of apparatus and chemical supplies; as a record of what has been done since the last exposition it was valueless. The dyestuff manufacturers, with their interesting and necessarily more or less spectacular displays, were conspicuously absent, and it was curious to listen to the comments made by the public on this fact, as well as to those made by dyestuff men themselves.

The public comment may be fairly summarized in some such way as this: "Where are the American dyes? Oh, well, you know, the war was over long ago, and we are getting all the good dyes we need now from Germany again. There isn't much trouble with dyes now; they are just as they were before the war, so there was no need to make any special displays of what has been done."

Can any thinking man, having the interest of the American dyestuff industry sincerely at heart, believe that a reaction in the minds of an all-informed public of this character can be anything but dangerous and inadvisable?

The progress in meeting the color needs of the nation during the past seven years goes for naught; the obstacles overcome and the difficulties conquered by sheer energy and pluck are unknown or forgotten, and the credit for the present satisfactory condition goes to the Germans and their well-cultivated fetish of chemical supremacy.

It may be true that those who use the dyes, the textile mills, the leather manufacturers, the paper manufacturers and others, know differently, but is there no responsibility to the public and to the press of the country whose appetite for misinformation so long as it makes good copy, is without limit?

The attitude of the dyestuff manufacturers themselves is largely responsible for this unfortunate public impression, and if the industry has still failed to "sell itself" to the American people these gentlemen have no one to blame but themselves.

This attitude may also be summarized, as expressed by most of them, as follows: "It would have cost us $5,000 or more to put up an exhibit, and we can put a good salesman on the road for a year for that amount of money. We don't make enough sales at these shows, or get enough inquiries, to justify the expense."

In other words they persist in regarding these expositions as sales factors, and not as publicity efforts to inform the people and press of the country of the

progress made, and the effectiveness of the efforts to make this country independent of foreign domination in what is unquestionably the most basic industry of all.

No exposition which makes sales the principal object can ever retain a permanent hold on public esteem as an evidence of industrial progress; it must inevitably degenerate into a fair, at which the passing people are importuned to buy anything that can be put up into a package and carried away. One has only to bear in mind the food expositions, the domestic science displays, and the business equipment shows, to realize the truth of this, and as the chemical and dyestuff manufacturers continue in their failure to realize the duty they owe—and especially is this the duty of the leaders in their ranks—to give an account of their stewardship to the nation as a whole, the more inevitably will these expositions become the resort of those who have trivialities to peddle.

And the more certainly will the industry find it impossible to convince an unenlightened Congress when the time comes—as it will come again before long—of its special needs, and its special title to consideration.

The above remarks take no account of the very excellent exhibit sponsored by the Synthetic Organic Chemical Manufacturers Association, which is mentioned elsewhere in this issue. This one exhibit in itself, however, did not begin to fill the place in the public mind formerly occupied by the dyestuff manufacturers.

THE DYES EXHIBIT AT THE CHEMICAL SHOW

THE one outstanding feature of the recent Chemical Exposition from a dyestuff standpoint was the display put on by the Synthetic Organic Chemical Manufacturers Association in co-operation with several other interested parties.

The slogan of this exhibit was "American Dyes Are Fast." This caption was prominently displayed in connection with various showings of dyed fabrics produced by various representative American manufacturers. The most interesting and instructive feature, however, was the showing of many gingham dresses which had been repeatedly washed and which were displayed side by side with other similar garments which were unlaundered. This demonstrated that the dyes suffered not at all in the washing process.

In order to bring this fact home most forcibly to the audience the garments in question were continuously washed in apparatus supplied by the American Laundry Machinery Company, and after being laundered were displayed on living models side by side with the unlaundered garments. Before the end of the Exposition the dresses thus used had been laundered over one hundred times. While the garments were being exhibited on the manikins a talk bringing out the fact that the dyes were of American manufacture and emphasizing their fastness qualities was delivered from the platform.

This is undoubtedly the sort of educational propaganda which should have been inaugurated several years ago. Had this been done, it would, we believe, in large part have offset the detrimental statements so frequently voiced by retailers to the effect that they could not guarantee the fastness of fabrics because of the necessity for using American made colors.

In our opinion this sort of an exhibition ought to be shown at every possible opportunity throughout the length and breadth of the country. It would be particularly effective if it could be shown in many large metropolitan department stores. If shown in such places it would have a dual effect: First, the education of the women buyers to the fact that American dyes can be depended upon; and second, it would effectively estop employees of these stores from resorting to the time-worn excuse that American dyes cannot be guaranteed. The latter effect is obvious, as should a clerk in the piece goods department offer any excuses for the dyes used it would be quite in order for the customer to refer to the exhibit in question appearing in the same store, whose purpose was to establish the fastness of American made colors.

Such an extended campaign of educational publicity would, of course, be an extremely expensive proposition, but we believe that if the Synthetic Organic Chemical Manufacturers Association and other interested parties were to get together on this proposition the necessary funds could be obtained and that the results would more than justify the expenditure involved.

METHOD OF DETERMINING THE DETERGENT ACTION OF SOAP

(*Continued from page 729*)

and a second filtration through another filter paper reduced the carbon number to the expected value.

The results with potassium oleate led to a few additional experiments, which seem to show that a carbon filtrate is more effective than the original soap solution in extracting fresh carbon black, and that likewise carbon black which has once been extracted produces with fresh soap solutions a filtrate of much higher carbon number than the original filtrate.

For the first experiments 8 g. of filtrate containing carbon from a 0.173*N*w potassium oleate solution was shaken up with a fresh quantity of 0.5 g. of carbon and filtered through fresh filter paper. In each case the carbon number went up manifold, being increased from such values as 0.76, 0.83 and 1.45 to 4.19, 4.48 and 3.09.

In the second series the carbon residues left on the filter paper from a previous filtration were treated with a

fresh sample of the original soap solution to see if any further carbon could be extracted, as there was a possibility that all the fine particles had already been taken through. However, the carbon number so obtained was invariably increased manifold. For instance, instead of carbon numbers 0.56, 1.14, 0.88, 1.46, 0.65 and 0.36, there were now obtained such values at 5.01, 3.59, 4.64, 4.39, 5.02 and 4.57, and a third extraction with further soap still gave quite high results.

These two results are obviously closely related, since the carbon, whether in the filtrate or in the residue, forms a sorption compound with soap, thus changing both the concentration and the composition of the solution. We have not had the opportunity of making a direct analysis of either of these quantities.

We are not pursuing this investigation further, in the expectation that the problem will be studied in America by the Fellow appointed by the Palmolive Company. However, now a general method of making a rapid and direct test of detergent action has been set up, it should be possible, by investigating different soaps, saturated and unsaturated, pure and admixed, and the effect of change of temperature, addition of salts and of excess of acid or alkali upon their detergent power, to explain fully the phenomenon of cleansing action.

The action upon carbon black may be to a certain extent specific and in so far not quite parallel to the effect on oily matter, or on emulsification, or on frothing; this would merely limit but not destroy the value of the direct information obtained.

SUMMARY

A method has been developed and standardized for the direct and rapid determination of the amount of finely divided carbon which various soap solutions carry through filter paper. This gives a "carbon number" characteristic of each solution which may be taken as a measure of the detergent action of this material.

It is shown that by a slight alteration of conditions the detergent action of a soap may be enormously increased. There is an optimum concentration in moderate dilution for which the effect is a maximum; very slight addition of either acid or preferably alkali greatly enhances the detergent power. Rise of temperature diminishes at first rapidly, then more slowly, the detergent power; but this may be completely overshadowed by the vital necessity of using sufficiently high temperature to dissolve the soap. Once in solution, there is surprisingly little difference between soaps as different as myristate and oleate.

In conclusion, our thanks are due to the Research Fund of the Chemical Society and to the Colston Research Society of the University of Bristol for grants for the purchase of materials used.

The Chemical Foundation Suit

Briefs Filed by Both Sides—Final Act in This Drama Opens at Wilmington October 8.

AFTER more than a year the curtain is about to be raised on the final act of the dye patent suit in Wilmington. On September 26 the United States Government filed its brief summing up the results of the evidence submitted. In it the Attorney-General renews the charges of conspiracy on the part of the American dye interests and states that at the time of the sale of the patents certain vague transactions served to blind President Wilson to the actual state of affairs. It further charges that the appointment of Frank L. Polk, counselor of the State Department, as agent to transfer the patents, was illegal; that Mr. Polk, though acting in good faith, was not in possession of complete knowledge of the transactions in which he figured. A contradiction of the latter charge is contained in Polk's testimony at the trial, in which he stated that he had assuredly not been deceived by anybody regarding the details of the transaction.

The Government brief, in addition, directly attacks the Foundation's claim that to seize and sell the German dye patents was necessary as a protective measure, the soundness of which would be apparent not only in times of war but also in times of peace. The brief states:

"The United States have not yet reached that point of national degradation where it must confiscate private property acquired in confidence in their good faith and integrity, and which its owners are unable to protect, in order to promote national prosperity or material gain. It will not seek to justify immorality by the wrongs of others, but will have the courage to do right. It is not a question of our obligations to the Germans, but to our own self-respect and national honor.

"The claim that these transactions may be justified on the ground that the ownership of these patents and other properties by the dye and chemical industries was necessary for the protection of those industries and to promote their development and prosperity is equally unsound in morals and in law."

Regarding the prices paid by the Chemical Foundation the document quotes Dr. Holderman's testimony, in which he placed a high valuation on the salvarsan, neosalvarsan, and novocain patents.

Scarcely a week after this brief had been filed the Chemical Foundation prepared and filed its side of the case. Point by point it assails the charges contained in the foregoing document, bringing forward certain pungent facts regarding the ethical and legal phases of the question.

It alludes to the vindication of the Textile Alliance, Inc., one of the alleged conspirators named in the Government complaint, denouncing as libelous the attack made upon the Alliance. The Foundation, with good effect, declares as "preposterous" the charge that the President acted in the dark and denies emphatically the

least suggestion of fraud and deception on the part of the American dye interests. This portion of the bill reads:

"The President acted with full knowledge in all he did in this matter. The bill is singularly indefinite. Who deceived the President and Mr. Polk is nowhere disclosed. Who the alleged conspirators were is nowhere set forth definitely and specifically; the long trial has not yet cleared up this strange mystery; the charges remain as nebulous as at the beginning."

In aiming at the statement in the Government bill that the litigation did not embrace questions of the future welfare of the country and its national defense, the Foundation argues "that the courts have no jurisdiction to review the determination of the President; that it was in the public interest that particular enemy-owned property should be disposed of otherwise than at public sale to the highest bidder, on terms and conditions of the disposition directed by him." The defense pertinently brings up the positive danger of such a public-sale to the dye industry in this country. It would be indeed simple, in such a case, for German agents to snatch up the bulk of the patents at their own price.

Garvin's part in the transaction, the bill maintains, was merely the continuing of plans laid out by Palmer, the former Custodian, in strict accordance with President Wilson's intentions. The bill points out that the main parts of the transfer and subsequent sale of the patents were the results of the President's approval of the entire transaction. Compatible with his policy regarding the German control of the organic chemical industry and the "vicious consequences of this control, . . . thoroughly known to and appreciated by him" he carried out his desires by developing the plan of selling the patents to American organizations.

The Foundation bill had recourse to previous testimony to dispute the statement that the price paid for the patents was far below their actual value as declared by Dr. Holderman; it goes on to say that because of investigations necessary to supply certain technical data not included in the patents themselves, and in consideration of the fact that the Foundation was compelled to issue licenses to American applicants and to limit its profits on the sales to 6 per cent, they judged the price paid was not less than adequate.

In a subsequent section of the bill there is introduced a strong bit of logic; it brings up the question of what the results would be were the Government, consistent with its action in the present case, to file suits against all the purchasers of alien property sold by the Custodian, instigating "a flood of litigations." This part reads:

"The Alien Property Custodian sold thousands of pieces of property of all descriptions, of every degree of importance and of enormous total value. These properties are held by thousands of individuals and corporations, run into every State and affect every industry, and have no doubt been the basis of almost innumerable transactions made in reliance upon the titles thus conveyed.

"The Government itself holds most valuable properties, including the great German docks and terminal facilities in New Jersey and thousands of patents covering important ordnance, naval and surgical appliances—all purchased from the Alien Property Custodian.

"Nevertheless, the Government's contention lays every single transaction of sale by the Alien Property Custodian under a cloud, and makes it possible to take into court each of them for adjudication as to the adequacy of the consideration paid. A flood of litigation is thus threatened. Thousands of titles are called into question, hundreds of thousands of transactions based upon those titles are threatened with invalidity.

"If such an affliction be visited upon our people, then in no other war in which we may be unfortunate enough to be concerned will it ever be possible to induce a business man to invest a penny in purchasing property in the hands of the Government by virtue of its right of capture. No one will want to buy such a lawsuit."

After reviewing both bills and carefully weighing the arguments and testimony involved it is apparent that when court opens in Wilmington Monday morning, October 8, it will be the signal for the beginning of one of the most important legal battles in the history of the American dye industry. The initial value of the German patents, $271,000, is a paltry figure when consideration is taken of the tremendous interests involved on both sides, of the huge sums spent by dye plants in this country to work the patents they bought with the assurance that they were being given an opportunity to develop an industry that should be strong enough to compete with foreign enterprises.

WARNER TO CONDUCT COURSES AT COLUMBIA IN TEXTILE CHEMICAL SUBJECTS

Columbia University has announced new courses in textile bleaching, dyeing and finishing. The classes are under the supervision of John F. Warner, superintendent of the Bronx Finishing Company, and an active member of the American Association of Textile Chemists and Colorists. These new courses are to enable mill operators and other students to obtain a thorough general knowledge of the subjects at a moderate fee.

The program of lecture subjects is as follows:

Bleaching and Dyeing

1. The chemistry of bleaching. After reviewing the reasons for the necessity of bleaching cotton cloth for most purposes, the various chemical reactions involved in bleaching will be studied.

2. Preliminary scouring operations. Wetting out, kier boiling, saponification.

3. Decolorization and agents employed. The use of chlorine. The part played by the air.

4. Various types of bleach—market bleach, printer's bleach, etc., degree of whiteness required. The length of time of European methods as compared to American.

5. Mercerization. Its two principal uses. Effect on the cotton fiber.

6. Defects in bleached goods. Loss of strength; stains, uneven dye and finish in subsequent handling.

7. General observations on dyeing. The various theories of dyeing.

8. Machinery used. The padding machine; the jigger; the continuous dyeing range.

9. Direct cotton colors and for what used. Their chemistry. The kinds of cloth on which they are usually used.

10. Basic colors and for what used.

11. Sulphur colors and their applications.

12. Vat dyestuffs and their applications.

13. Insoluble colors and how produced. Mineral khaki. Iron buffs for shade cloths. Ice reds. Indigo blue.

14. Various types of black dyed fabrics. Logwood black. Comparison of prussiate and copper aniline blacks. Developed blacks for rubberizing.

15. Defects in dyed goods. Uneven and spotty dyeing; variations in shades; reasons for changes which may occur after dyed goods are cased and stored.

Printing and Finishing

1. The underlying principles of printing of textiles.

2. Block printing. Its history. Reasons why still employed on some fabrics. Mode of procedure.

3. Machine printing. Multi-color printing. Duplex or registered printing. Intermittent printing.

4. Basic, alizarine and vat printing compared as to cost, fastness, etc. Fabrics suitable for each of these classes of dyes.

5. Blotch and discharge printing.

6. Defects in printed goods. "Doctor" streaks; shadiness from side to side of a printed piece; blanket defects.

7. The chemistry of sizing.

8. Agents employed in starching and sizing. Starches, dextrines and gums. Soaps and oils and their uses.

9. Conditioning. Its relation to the final finished result.

10. Plain calendered finishes. Sheetings, print cloths, etc., with special reference to their ultimate uses.

11. Imitation mercerized finishes. Sateens, alberts, etc. Comparison of full mercerized and imitation mercerized results from the consumer's viewpoint.

12. Summary of bleaching.

13. Summary of dyeing.

14. Summary of printing.

15. Summary of finishing.

These courses are offered in response to a request for instruction in the practical processing of cotton piece goods fabrics from the time they are woven until they are ready for the consumer's needs. They are intended for those interested in the converting, seasonal styling, or merchandising of cotton piece goods, as well as for those engaged in theoretical or practical textile coloring and printing. They are so designed that anyone who has had the equivalent of an ordinary high school course will be able to follow the lines of thought readily. They will not be given for less than fifteen students.

For further details address the Secretary of Columbia University, New York, N. Y.

NEW DU PONT COLORS

Sulfogene Olive Drab GX and Sulfogene Olive Drab RX are two types of sulphur colors that have just been announced by E. I. du Pont de Nemours & Co.

These two products are very adaptable for the production of Olive Drab shades. Their solubility is excellent and the exhaust very uniform, making them adaptable for use in continuous machines.

Another product recently placed on the market by this concern is a new direct color under the name of Pontamine Fast Blue SL which is of particular importance on account of its resistance to light.

In addition to being suitable for cotton, the product is adapted for paper on account of its excellent fastness to light. It does not require after-treatment, as this method does not give any increase in fastness to light, and only slightly increases its fastness to washing.

CONFUSION IN TEXTILE CONDITIONS

The National City Bank Bulletin reports uncertain conditions in textiles as a result of the present crop and market situation.

In cotton goods this results from uncertainty about the size of the crop of raw cotton and whether consumers will buy the goods freely on the basis of present costs. The mills could book plenty of orders at prices that would have been acceptable two or three months ago, but they cannot cover their requirements for raw material and get out even on that basis now. Illustrating changes since last April when in a scare about the crop raw cotton went above 31 cents per pound, 64/60 print cloths which sold then as high as 11¼ cents dropped to 8⅜ cents and are now about 10 cents, although within the last month cotton has sold above 30 cents and at this writing is a little under 29 cents. Despite the difficult situation cloth production is much above what it was several months ago.

The consumption of cotton in August was 491,604 bales, against 461,575 in July and 527,404 in August last year.

In woolens, men's wear is having a very slack time, but dress goods are in good demand. The trouble in men's wear is said to be due to the backward spring which left a lot of spring goods on dealers' hands, which are now in the way of new spring business. The silk business has been affected by the destruction of raw silk in Yokohama, and the situation is yet unsettled.

YOKOHAMA PORT REOPENED

A wireless message received recently by the Silk Association of America from the Raw Silk Association of Japan announces that the Yokohama market and port were opened September 17, and will remain open hereafter. The news indicates a renewal of activity in the raw silk trade, although no further details could be learned. It is thought, however, that in the absence of housing and shipping facilities, it will still be some time before shipping in any volume can be routed to the port.

Tapestry Yarn Printing*

By LOUIS J. MATOS, Ph.D.

Mechanics of Operation Described—Preparation of Color Paste—Color Mixing—Preparation of Yarn for Printing—Various Recipes

IN the manufacture of carpets, next in importance to the dyeing of yarns for the production of brussels or velvet grades, is the printing of yarn for the so-called tapestry brussels. This process is not well known to the general public, although it is of great importance for producing many of the cheaper stair and floor carpets. It is a particularly interesting process, since the colored design is printed directly on each individual warp thread that is eventually to appear as the face of the carpet. In printing these warp threads, the space occupied by each color is somewhat longer than it will appear in the finished carpet; this is necessary in order to allow for the proper "take-up" in weaving.

Yarn for axminster, brussels, and other carpets is dyed in skeins or hanks, with such colors as the design calls for, usually not more than five for each pattern, hence the name "5-frame" body brussels, etc. With printed tapestries, however, the choice of colors is not limited, and may greatly exceed the above number.

A carpet design made for tapestry printing provides for the coloring of each single warp thread, with that portion of the pattern through which the thread passes. Each warp thread is printed in succession with all the colors belonging to it. It is therefore seen that every warp thread differs from every other warp thread, except where there is a repeat of the pattern.

Yarn printing requires the use of large wooden drums of special construction. These drums may be 8 feet in diameter, and 3 or more feet in width. The yarn is evenly wound around these drums to the thickness of several layers, and to the surface of which the prepared color is applied by means of a small color-box that travels across the face of the drum and immediately under it. There is a box for each color. In the color-box is mounted a hard rubber wheel about 8 inches in diameter, the printing face of which varies according to the width of stripe desired, usually about three-fourths inch, and frequently less. This face is slightly concave like the runner of a skate, so as to conform somewhat to the curvature of the large drum. This concave face permits a reasonably sharp edge to the printed stripe.

As this color-box travels from side to side, the roller which is partially immersed in the printing paste, leaves a stripe of color which is applied with such pressure as to force the color paste through the several thicknesses of the yarn. According to the number of trips this roller makes, the stripe is printed either narrow or wide, the increased width being due to a slight motion given to the large drum, the control of which is always regulated by the printer, and strictly in conformity with the design board which is constantly in view. In printing a "drum," each color is applied in proper order, that is, all red stripes of one shade are printed in their proper places, then the blues, greens, yellows, blacks, etc., until the particular warp thread is completed. All other warp threads for the same design are printed in the same manner. An error in printing a stripe means the rejection of that particular "drum" of yarn, which is generally utilized by dyeing black, and worked into plain carpets.

The colors used are ordinary acid dyestuffs that are made into a thickened paste with wheat flour, together with starches, such as sago, and frequently also with yellow dextrine. The flour is first made into a paste with water and a suitable antiseptic, usually salicylic acid. For fixing the color on the wool, oxalic acid is generally employed, but some few dyes require small quantities of other acids, such as sulfuric, acetic or tartaric. Oxalic acid is preferred for the reason that it is low in cost, and has but little, if any, action on the printed yarn when the latter is steamed.

After the yarn is printed, it is removed from the drum

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and allowed to become "air dry" by hanging in a shed or other covered place where there is free access of air. It is then placed on large wooden frames that are diagonally strung with twine, and placed in the steam-box where it is subjected to the action of moist steam for about half an hour at low pressure. This steaming effects the actual dyeing of the yarn at the place where the color is printed. If the steam is too moist, there may be danger of some of the printed colors running into those adjacent, thereby spoiling the sharpness of outline desired in the finished carpet. This is guarded against by regulating the condition of the steam in the box, and also by making a selection of such dyes as possess a lower rate of solubility. For example, certain of the so-called level-dyeing colors, which owe their property of yielding extremely level shades to their slow absorption by the wool in an ordinary dye-bath, would be found generally unsuitable for printing on account of running or "bleeding" before they become fixed on the wool under the influence of the steam. Relatively rapid dyeing colors are more desirable for this particular purpose.

Color mixing for yarn printing is most particular work, and frequently a number of trials must be made by the foreman before the correct proportions are obtained. These must be first worked out with small quantities, followed by the full quantity for the entire job, with each trial fully steamed, washed, dried, and compared with the standard before the batch is ready for use by the printer.

Sample swatches for this work are made by taking about 25 or 30 strands, about 1 yard in length, of identically the same kind of yarn that is to be printed, tying them at one end, and attaching this tied end to a hook, the loose or untied ends free to be held in the left hand, and with a brass or bronze spatula, spreading some of the printing color to be tested upon it. Several strengths are made by diluting definite quantities of the full-strength color with fresh flour paste. As an example, a "color' would be made up with:

Croceine Scarlet	½ ounce
Oxalic Acid	½ ounce
A little water, and flour paste to make	8 ounces

equivalent to an "8 ounce color," i. e., 8 ounces of dry dye per gallon of finished printing paste.

When the dye is completely mixed and dissolved, a 4 or 5 inch length would be spread on the yarn for No. 1 shade, then 4 ounces of the above would be diluted with 4 ounces of flour paste and printed for No. 2 shade. Four ounces of No. 2 is diluted with 4 ounces of paste for No. 3, and this again diluted in the same manner for No. 4. These prints then represent color-shop weights of 8 ounces, 4 ounces, 2 ounces, and 1 ounce of dye per gallon of "color," and are so designated. It is readily seen that there can be no comparison between shades obtained by printing and shades obtained by dyeing—the former being produced by a definite quantity of dye in a fixed volume of paste, while the latter result from dyeing a definite percentage of color calculated on the weight of the material dyed. Shades produced by printing may be matched by dyeing and *vice-versa*.

Color mixers are not in the habit of using straight dyes in making their stock color pastes, but compound and designate them as "standards," taking whatever is needed from each "standard" to make the final printing color. Then a final color may contain as many as six standards in various proportions. This is important to understand, since it must be realized that when the final color is delivered from the color shop to the drum-room, the color-mixer has lost control over it. The color-mixer is not in the position of a dyer who can observe how his shades are coming up. The color-mixer and drum printer can only see the result of their work after the yarn has been steamed, washed, and dried. If the printed shade is "off," there is no remedy except to dye it black, since to run it in the pattern would spoil the entire effect. The color-mixer must be continually testing every mix that is made, not only of his standards, but also of the actual printing colors.

In well regulated color-shops, immense numbers of these printed yarn swatches are made each week, and nearly all are preserved for future use, the record of the formula being entered in the formula book, or on cards, while the swatch is either pasted in large books for reference, or frequently, put into the small pasteboard tubes so that the cut and uncut ends of the yarn may be exposed for inspection.

In making up the final printing color from an established formula, the same routine is followed, and in general, nothing is taken for granted. When a new dye is to be substituted for one already in use, even greater care is necessary in making the tests, since it means that introducing a new dye, the formulas of possibly several hundred other colors will need to be changed.

As previously mentioned, in making trial batches of color for yarn printing, a good working basis is to use 8 ounces of dye per gallon of flour paste. Of course, a gallon is far too great a volume to make up for trial tests, but proportionately smaller quantities are convenient, say one pint or half pint. On this basis the equivalents are:

1 gallon	of "color" per	8 ounces	of dye
½ gallon	of "color" per	4 ounces	of dye
1 quart	of "color" per	2 ounces	of dye
1 pint	of "color" per	1 ounce	of dye
½ pint	of "color" per	½ ounce	of dye
¼ pint	of "color" per	¼ ounce	of dye

The artist's design is made on "weavers' paper"; only one section of it being used at a time. This is pasted on a smooth board, usually 8 or 10 inches wide, and of such length to take an entire unit of the complete pattern. For durability, and to permit cleaning, it is given a coat

of shellac varnish. Each color called for by the design is indicated by a number, actually painted in small figures on the design, and which correspond to the one in the color-mixer's formula book. It must not be supposed that the shade or tint actually painted on the design is the exact shade to be duplicated. The selection and blending of the shades are always made in the designing room from hundreds of printed yarn samples that are conveniently held in the paper tubes previously mentioned. These tubes permit the designer to group the colorings conveniently in his hand so that he can see them more effectively, and make a more satisfactory choice.

The design board above mentioned, is attached to one side of the printing drum, fastened up to the frame of which is a rule or straight-edge, permitting the printer to keep the warp thread that he is printing constantly in view. Each horizontal line on the design board corresponds to a notch on the large control gear which regulates the circumferential motion of the drum. One notch corresponds to one space; therefore, if a stripe is to be printed across the drum, say, three notches wide, the drum is revolved accordingly, while the color-box makes corresponding trips from side to side, leaving its band of color paste.

Preparation of the yarn before printing requires some attention to detail. Oily or greasy yarn cannot be successfully printed, because the oil acts as a resist to the color, preventing proper penetration with resulting unevenness. The yarn must be scoured clean and rinsed free of all traces of soap; it is then ready for sulfuring in order to bleach it as white as possible. At best, sulfuring is disagreeable, but this process still remains the cheapest. Sulfur bleached yarn must be given a good wash with water containing a small amount of sodium bisulfite to neutralize any traces of free sulfurous acid that remain and finally rinse well. These operations are necessary, otherwise traces of sulfurous acid in the yarn will react upon some of the colors.

The color-shop is equipped with a battery of steam jacketed copper or monel metal pans in which the colors are compounded. These pans should be tilting so as to be readily emptied. The storage facilities for standards consist chiefly of large barrels, or preferably, covered stoneware crocks of various capacities, while the containers in which the finished color is sent to the drum-room are generally large stoneware pitchers or jugs.

Besides the foregoing, the most important part of the color-shop is the equipment for making the thickening. As a general rule it consists of two, sometimes three, large wooden vats in which paddles revolve to keep the mass well stirred during the cooking. One of these vats is always in service, while the other is being charged with the flour to make a fresh batch. For a 100 gallon batch of flour thickening, there is used the above quantity of water, and 300 pounds of sweet flour that should test relatively high in gluten, and from 15 to 18 pounds ammonia alum.

During the making of the paste, actual boiling should not be permitted, and also during the actual use of the thickening in the color pans while compounding the colors, boiling is to be avoided. A temperature of 180 to 190 deg. Fahr. is sufficient.

Reference has been made to the use of flour that tests relatively high in gluten as being most desirable for color thickening. A flour that is low in gluten content does not make a satisfactory thickener, and it is for this reason that straight starches are not extensively used in carpet printing. Starches give a bulky thickening that does not possess the required body. A musty flour, or one that is a mixture of sound and musty flour, though costing less, is not suited since there is a possibility of the presence of certain micro-organisms likely to cause the thick paste to liquefy over night, and the batch is then of no value. This does not imply that some flours, unsuited for bread making, cannot be used in the color-shop. For this kind of textile printing, ordinary flour is quite suitable, but it is of little value when textile fabrics of comparatively fine texture are printed from engraved copper rollers.

After each color is compounded, it is strained to remove any lumps of flour or other ingredients that might accidently have escaped softening. The finished colors are used cold, warm color pastes are likely to be too thin in consistency, thereby yielding shades that are not as full as when the color is cold. On the other hand, the colors must be so stiff that they will adhere readily to the hard rubber printing wheel in the color box, and yet have such a degree of fluidity as to run slowly.

The standard colors, those that are used for compounding the actual drum-room colors, are usually compounded with dextrine and the necessary acid. They are kept covered to prevent evaporation and to protect them against possible splashing of other colors and from loose dye dust. In making relatively large batches of color, the known quantity of dry dye is weighed out and dissolved in a small amount of water and acid in one of the metal pans, then some dextrine is added, and the whole diluted with the proper quantity of flour thickening. After the mixture has been thoroughly stirred it is tested for shade. If shading colors are needed to "bring it up," they are selected from the stock standards.

The following recipes illustrate the detail as outlined in the foregoing.

For National Alphazurine A and 2G, National Alizarine Sapphire, and National Alizarine Sapphire FS.

(Per gallon of color standard)

	Ounces
Dye	7½
Water	57½
Dextrine	41¾
Oxalic Acid	2½
Water	18¾

For Wool Oranges, such as National Wool Orange 2G Cryst., National Wool Orange A. Conc. and R Conc.

(Per gallon of color standard)

	Ounces
Dye	3¾
Water	42½
Tragacanth 65/1000	28
Dextrine	25
Oxalic Acid	3¾
Water	25

For National Fast Crimson GR and R, National Fast Fuchsine 6B and G, National Wool Navy Blue B, National Azo Bordeaux, National Wool Yellow Extra Conc., National Acid Fuchsine D, National Fast Red S. Conc., National Azo Rubine Extra, National Metanil Yellow 1955, National Wool Red 40 F, and National Quinoline Yellow.

(Per gallon of color standard)

	Ounces
Dye	5
Water	48¾
Tragacanth 65/1000	28
Dextrine	25
Oxalic Acid	2½
Water	18¾

For National Azo Yellow A5W, National Fast Acid Green B, National Fast Wool Blue R and B, and National Buffalo Black 4AB.

(Per gallon of color standard)

	Ounces
Dye	2½
Water	47½
Acetic Acid, 8 deg. Tw	12½
Tragacanth 65/1000	65½

For Acid Scarlets, such as National Brilliant Scarlet 3R, and National Croceine Scarlet MOO.

(Per gallon of color standard)

	Ounces
Dye	5
Water	43¾
Tragacanth 65/1000	28
Dextrine	25
Oxalic Acid	2½
Water	18¾
Acetate of Alumina 18 deg. Tw	5

For Navy Blues, compounded with mixtures of Acid Violets and Acid Greens.

(Per gallon of color standard)

	Ounces
Dye (according to proportions)	7½
Water	61¼
Dextrine	38
Oxalic Acid	2½
Water	18¾

For Naphthol Green.

(Per gallon of color standard)

	Ounces
Dye	7½
Water	50
Tragacanth 65/1000	28
Dextrine	25
Chlorate of Soda	3¾
Water	7½
Acetic Acid 8 deg. Tw	6¼

The above recipes are typical of the general line of printing colors, and where they are used in relatively small quantities the use of a paste made of gum tragacanth is permissible. For larger quantities, the tragacanth is substituted by the flour paste. To make combination shades with these, the color mixer uses whatever quantity his trials call for, using as thickener for the large batch the necessary amount of flour paste. These "standards" are uusually much stronger in shade than the design colors call for, and consequently will stand a considerable amount of dilution or reduction.

With the foregoing, almost every shade required by the designer of tapestry carpets may be obtained with the possible exception of some very delicate tints that are but seldom called for. Such shades may be produced with very small quantities of some special dyes that are found in most color shops.

After printing, air-drying, and steaming to fix the color, the yarn is washed to remove from it all traces of the flour thickening and other chemicals used in the colors. This washing must be so thorough that the yarn is absolutely clean. If the proper selection of dyes has been made, and the steaming has been correct, the colors on this yarn will be full-bodied, clean and sharp, with no evidence of one color running into its neighbor. The washing should be only so long as is necessary to remove the thickening and no longer. Excessive washing is likely to be detrimental to the yarn which is in the form of very large skeins or hanks equal in length to about 1½ times the diameter of the drum on which they were printed. This requires care in handling so that there will be no appreciable stretch of the pattern as printed which would cause troublesome work in the "setting room," that department of the mill where the printed warp threads are brought together in their proper order and position preparatory to being wound on the beam for weaving.

At all times the complete solution of the dye used is necessary. Any undissolved particles that pass into the finished color are likely to appear in the printed yarn as distinct specks or other unevenness. While this is not a serious defect in very deep shades, it is the cause of blemishes that show quite distinctly in the lighter shades. To prevent specks in the color, the dyes should be completely dissolved in the smallest volume of hot water and strained into the mixing pan.

Indigo and Its Application

Part II

Cotton Dyeing—Various Recipes—Indigo Vat for Cotton—Methods of Dyeing—Machines Employed—Combination Dyeing on Cotton—Silk, Linen and Jute

By PHILIP S. CLARKSON

H. A. Metz & Co., New York City

Cotton Dyeing

WHILE the principle of cotton dyeing with indigo is the same as that of wool, the vats used for this differ both in strength and assistants used.

The three vats in common use for cotton dyeing are the Copperas Vat, the Zinc-Lime Vat and the Hydrosulphite Vat.

Copperas Vat.—Although it is usual to reduce the indigo in the dye kettle, it is better to carry out the reduction in a more concentrated solution, as the reducing agents act more rapidly and the loss of indigo is less. The reduction generally requires about three hours, and time can be saved if the chemicals are mixed together in the evening and allowed to stand overnight. The proper proportions are:

10 pounds Indigo powder.
40 pounds Copperas.
50 pounds Lime.

or

50 pounds Indigo 20% paste.
40 pounds Copperas, and
50 pounds Lime.

The copperas should be dissolved in hot water and be added to the indigo previously made into a paste with water, and then the slacked lime added and as much water as is necessary to make the mixture of indigo, lime and copperas to a thin paste. The temperature of this stock liquor should be about 110 to 130 deg. Fahr. It is then well stirred and allowed to stand until the reduction is complete.

Color Vat.—These vessels may be either round or rectangular, made of either wood, or stone with cement joints, from 70 to 100 inches deep and from 30 to 40 inches across. On account of the depth of these, in order to make the handling of the material easier they usually set below the level of the floor. Before adding the reduced indigo to the dye kettle, the oxygen in the water should be absorbed, which is done by adding 4 pounds of lime and 2 pounds of copperas for each 250 gallons of water, the lime being slacked and made into milk with water. The vat is then stirred up and allowed to stand for one hour, when the stock liquor may be added. The whole is thoroughly stirred and allowed to stand for two or three hours. When the sediment has settled, the liquor should have a brownish-yellowish appearance, and on stirring blue veins should show on the surface. The blue scum or flurry should be removed before dyeing. As in the other vats, it is necessary to carefully observe the appearance of the liquor, and if the vat is greenish the indigo has not been completely reduced, and therefore more copperas should be added. If the vat is dark it is not sufficiently alkaline and more lime will be required. It is necessary also to keep the proper proportion of all the ingredients, as an excess of lime will make the vat dye too slowly, while too strong a vat will deposit the indigo too rapidly on the fiber and the dyeings will not be fast. If the vat is to be run continuously, which is not often the case with the copperas vat, the stock liquor may be added in the evening; after stirring, the vat is allowed to stand overnight. This vat is principally used for dyeing skein yarns and cloth that has been printed with resists. In warp dyeing and continuous piece dyeing it has been replaced by the other vats.

Zinc-Lime Vat.—This has the advantage over the copperas vat that it contains a smaller quantity of sediment, the dye kettle and the method of working being generally the same as the former. As before noted, it is better to reduce the indigo in a concentrated solution. For this use:

10 pounds Indigo powder.
6 pounds Zinc Dust.
20 pounds Lime.

or

50 pounds Indigo 20% paste.
6 pounds Zinc Dust.
20 pounds Lime.

The zinc dust is stirred with 5 gallons water and added to the indigo, which has been ground with water to a paste, and last the slacked lime is added. This mixture is made up to 20 gallons and kept at a temperature of 115 deg. Fahr. and stirred frequently for five or six hours, when the reduction should be finished.

Before adding the reduced indigo to the dye kettle the water should be corrected with 2 pounds of lime and 10 ounces zinc dust for each 250 gallons; then the stock liquor is added. The zinc lime vat in proper condition has the same general appearance as the copperas vat, and should be clear and amber colored with

a good flurry and show blue veins on stirring. If the vat contains too much zinc dust the hydrogen is generated too rapidly and the sediment, instead of settling, remains in the liquor and causes a dark appearance with foam on top. This condition may sometimes be removed by stirring, but if this does not give the proper result more indigo should be added to absorb the excess of hydrogen.

Hydrosulphite Vats.—The hydrosulphite may be prepared in several ways: either by producing the hydrosulphite in the presence of the indigo; and this, immediately reacting on the latter, reduces it; or by the addition of already prepared hydrosulphite to the indigo. The former vat is commonly known as the Zinc-Bisulphite-Soda vat. It has one disadvantage of containing considerable sediment. To prepare this the following proportions are used:

50 pounds Indigo paste
5 gallons Milk of Lime
containing 20% lime are mixed with
3 gallons Water
and into this mixture
5 gallons Bisulphite of Soda 75 deg. Tw.
previously mixed with
7 pounds Zinc Dust
and allowed to stand for ten to fifteen minutes are stirred.

The mixture should then be made up with hot water at 150 degrees and stirred again. In about two hours the indigo will be reduced and the solution should show the usual yellow color. Care should be taken not to stir too frequently, as this will oxidize the hydrosulphite and prevent the proper reduction of the indigo. On account of the sediment this vat requires about the same dye kettle as the other vats. It is principally used in England.

Hydrosulphite Vat.—This vat has the great advantage over the copperas and other chemical vats of containing absolutely no sediment. It may be used for all kinds of dyeing, and it is particularly indicated where the dye bath must be perfectly clear, as in the dyeing of piece goods, warps, cotton, etc., in machines. As with the other vats, it is better to make up a stock liquor and add this to the dye kettle.

Proportions to be taken are:

10 pounds Indigo powder, or
50 pounds Indigo 20% paste,
are mixed with
2½ gallons Warm Water.
3¾ gallons Caustic Soda 76 deg. Tw.
and stirred.
The temperature is raised to 105 deg., and
8 gallons of Hydrosulphite
are stirred in.

The temperature should remain constant for one to two hours, and if the solution is not clear yellow a further addition of ½ to 1 gallon hydrosulphite is made. The hydrosulphite may be made from zinc dust and bisulphite of soda. This hydrosulphite solution may be prepared as follows:

35 gallons Warm Water 86 deg. Fahr.
are put in a suitable barrel and
108 pounds Sodium Bisulphite 75 deg.
Tw. added.
12 pounds Zinc Dust
previously made into a paste with warm water,
are stirred in during an hour.

The mixture is allowed to stand for one hour, and 8 pounds of 100 per cent caustic soda are added and the whole allowed to stand again. The clear solution is hydrosulphite, and is ready for immediate use.

Color Vat.—The water is corrected as usual by the addition of 1 quart hydrosulphite to every 250 gallons of water and allowed to stand an hour. After the addition of the stock solution the vat is then stirred and allowed to stand for several hours, and it is then ready for dyeing.

Fermentation Vats.—In some cases this form of vat is used for dyeing cotton; but while it is more difficult to handle than the chemical vats, it has the advantage of giving stronger and brighter shades. Besides, it gives also the so-called indigo odor to the dyed material, which in some markets is absolutely necessary.

The amount of indigo used for these vats is more than for wool, as they run at about the same strength as the chemical vats. The vat may be warmed with artificial heat, and as the means of reduction various substances which ferment easily in alkaline solution are used. Among these are bran, flour, rice, syrup, etc. A vat which gives good results is made up with:

50 pounds Indigo paste.
24 pounds Bran.
25 pounds Calcined Soda.
16 pounds Madder.

The vat should be heated to boiling and cooled down to about 140 deg. Fahr. and the materials added. After the fermentation is complete, the vat, as in the case of the wool vats, is sharpened with lime or soda. If the fermentation does not start satisfactorily it is well to add about 10 pounds of syrup.

Cotton Dyeing with Indigo Vat and Indigo Vat for Cotton

Indigo vat can be used to great advantage in cotton dyeing and, as it avoids the reduction of the indigo in the stock vat, a great saving of time and labor is

effected. It is especially suitable for the hydrosulphite and also for the fermentation vats. In the latter case, as the indigo vat furnishes a clear solution of reduced indigo, it is only necessary to add to the color vat sufficient reducing materials to prevent oxidation by the air. In this way there is a large reduction in the amount of sediment, and the proper maintenance of the vat is made much easier. In working the vats with this solution, all that is necessary is to add the reducing agents, stir up, allow to stand one hour, and then, after adding the necessary amount of indigo vat, with one hour's longer standing, the vat is ready for use. These proportions of materials have been found to give good results:

Hydrosulphite Vat.—For 250 gallons of water add 6 to 7 pints hydrosulphite, after one hour the necessary amount of indigo vat, stir thoroughly, and then add sufficient caustic soda to change the bluish-green color of the vat to yellowish green, and after thoroughly stirring again it is ready for use.

Fermentation Vats.—For 250 gallons of water at 110 deg. Fahr. add:

16 pounds Bran.
10 pounds Flour.
2 pounds Sodium Carbonate, 58%.

After two or three hours the fermentation should start, and 16 pounds indigo vat are added. The whole is stirred well and allowed to stand one to one and one-half hours. The vat should then be ready for dyeing.

Indigo Vat for Cotton.—While indigo vat can be used for both wool and cotton, where the latter only is to be dyed the use of indigo vat for cotton is recommended, especially for piece dyeing. With these the older methods of reduction of the indigo are not needed, and the dyeing operation is much simplified.

Strength of the Vat.—For medium and dark blues from 12 to 15 parts of indigo vat for cotton to 1,000 of liquor will be necessary, while for light blues the proportion should be reduced to 5 parts. With the full strength of liquor, dark blues can be dyed in two runs on the continuous machine. Medium blues can be colored in one run, or in two by speeding the machine. Light blues require one to two runs in the weak liquor.

Preparation of the vat:

For each 100 gallons of vat liquor the following stock liquor is prepared:

26½ pounds Indigo Vat for Cotton.
1½ gallons Caustic Soda solution 66 deg. Tw.
4 gallons Hot Water 160 deg. Fahr.
7½ quarts Hydrosulphite.

The vat is stirred for several minutes, and when the proper condition is reached, which is indicated by a yellowish olive-green solution, the dyeing may be started.

To keep the vat in proper condition, a further daily addition of 1 to 2 pints of hydrosulphite is necessary. This should be added in two portions, at noon and evening. The liquor should be replenished every day to keep the strength constant, and it is better to add the fresh liquor also in two portions. The amount necessary naturally depends upon the character of the material, and may be varied accordingly.

After dyeing, a thorough washing is sufficient; but printed material is often passed through an acid bath at 1½ deg. Tw.

If dry material is used it must previously have been well boiled out and bleached, which will insure the equal wetting of the goods in the passage through the vat. For practical reasons, such as saving drying and on account of the damp material carrying less air into the liquor, it is best to work with wet goods which have been well squeezed.

Dyeing Methods

Raw Cotton.—The dyeing of cotton in the raw state is so difficult that it has little practical value, and only in exceptional cases is it used. It is necessary to use a dyeing machine, as in the open kettle it collects in lumps, which interfere with the proper handling and also cause great waste in carding. It can be dyed in a machine similar to that used for slubbing, and the hydrosulphite or filtered zinc vat can be used.

The cost of dyeing raw cotton is very much greater than that of yarn or piece goods.

Cotton Yarn in Skeins.—Before dyeing, the yarn must be boiled out well, hydro-extracted and entered in the vat while wet. Care must be taken to work it evenly and wring it out well. The length of time in the vat is regulated by the depth of shade and the strength of the vat. Faster and more level shades are produced by dipping first in weak vats and then in stronger; as many as eight or ten dips may be given, the yarn being wrung out and oxidized in the air between each. After dyeing, the yarn is soured with oil of vitriol or muriatic acid at 2 deg. Tw., except when the hydrosulphite vat is used. With this vat the acid bath is not needed, a simple washing in water being sufficient to remove the caustic soda of the dye liquor.

Warps.—These are usually dyed in chains, being run through the vat on movable frames with rollers. These frames are arranged so they can be moved from one vat to the other. The warps are first boiled out, then run through a weak vat before using the stronger ones. They are well squeezed out between each dip, and after dyeing are soured and washed the same as skein yarn.

Recently an improved machine for dyeing warps has been introduced by the manufacturer of the well-known Fries Dyeing Machine.

The method of dyeing used in this machine is to take the dry warps without previous boiling and run them through a box which contains sheaf pulleys set at an angle and a partition arranged so that the warps have two dips in the first compartment and ten or more in the second or larger. A suitable rubber roll is so placed that the warps are thoroughly squeezed after each immersion. From the box the yarn may be suitably oxidized by exposure to the atmosphere by running over the reels of the machine, and then dried on the cans. If it is desired to wash the yarn another similar box is used, and the yarn is then dried on the cans.

The first compartment of the box contains a solution of indigo white—the manufacturer recommends the zinc-lime vat—the strength being made suitable for the shade desired, and the second contains a solution of indigo in sodium hydrosulphite, the amount of indigo in this being 10 per cent of the amount in the first compartment. In the process the fresh reduced indigo solution is padded on the dry yarn which passes through the solution at constant speed under constant pressure of the squeeze rolls. The padded yarn then runs through a solution of dilute sodium hydrosulphite indigo solution and is given ten or more dips in this. The practical result is that the padding serves as a continuous uniform feed of reduced indigo of the strength proportioned to the required shade, and the second bath completes the dyeing with the same advantageous results as would be obtained in ten or more dips in weak hydrosulphite vats.

The great advantage of the process is the fact that the whole operation from the white yarn to the finished product is continuous, thus effecting a great saving in labor cost, and the result is superior to that produced in the ordinary machines.

Piece Dyeing.—Piece goods are dyed either in the dipping vat, as it is termed, or in the continuous dyeing machine.

When the dipping vat is used the goods are stretched on frames by fastening the selvedges. These frames are then sunk in the dye liquor and let stand for fifteen or twenty minutes, the liquor being occasionally stirred by means of a rake. The frames are then raised and the blue oxidized in the air.

This method is used for heavy goods and material which has been printed with resists, the heavy material requiring a longer immersion than can be given in the continuous machine, and the friction of the rollers in the latter destroying the printed resists.

In the continuous roller machine, which is generally used, the goods are run through the vat on rollers arranged so the goods run several times from the top to the bottom of the vat liquor.

On coming from the bath the goods are well squeezed and then run over rollers in the air for the purpose of oxidation.

One, two or several runs may be given, according to shade desired. After the necessary runs the goods are rinsed and soured, as in case of yarn.

Combination Dyeing on Cotton

Various methods of reducing the cost of dyeing cotton with indigo have been tried by the use of other dyestuffs in combination with it. Different ways of using these have been suggested, some of them being mixed in the vat; others are used for topping the indigo dyed goods, and some are used for bottoms, the material being passed through the vat after dyeing.

An example of the latter is the use of Melanogene Blue B as a bottom. This will increase the depth of shade very materially, and the cost is not excessive.

However, since the manufacture of synthetic indigo on a large scale the cost of pure indigo dyeing has been so greatly reduced that, except for peculiar effects, combination dyeing will probably go out of use.

Silk, Linen and Jute in the Indigo Vat

Silk is not often dyed in the vat. As lime will make the fiber brittle, the hydrosulphite vat is used, and the use of indigo vat is recommended on account of the small amount of alkali required.

Linen and Jute.—These are dyed in the vat by dipping. They require a very long time in the dye bath to secure penetration, and therefore the continuous machine is not suitable. In starting, a very weak vat must be used. The usual kind of vat for this purpose is either the copperas or zinc-lime vat. The methods of handling are the same as for cotton.

(End of Part II; Part III will follow in an early issue.)

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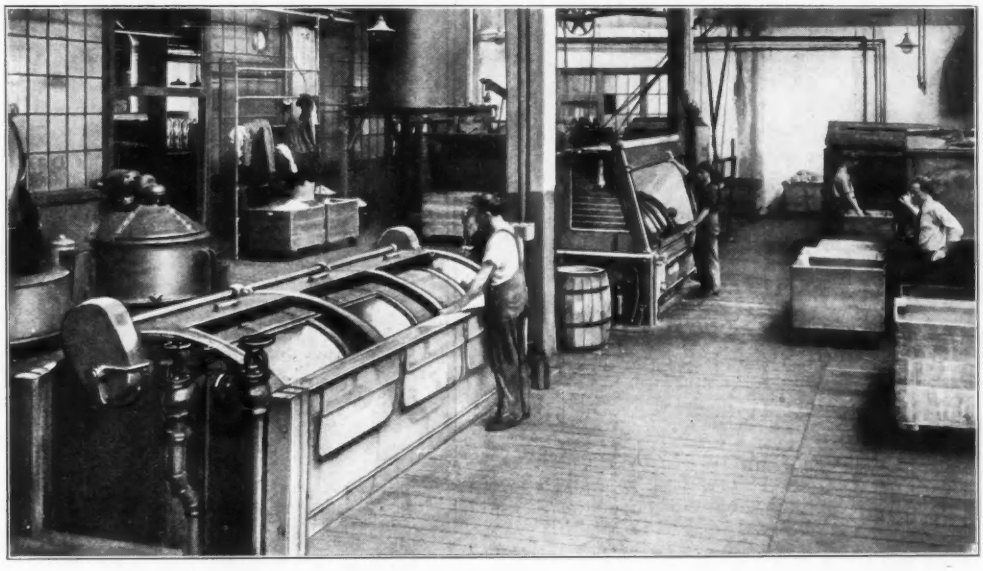

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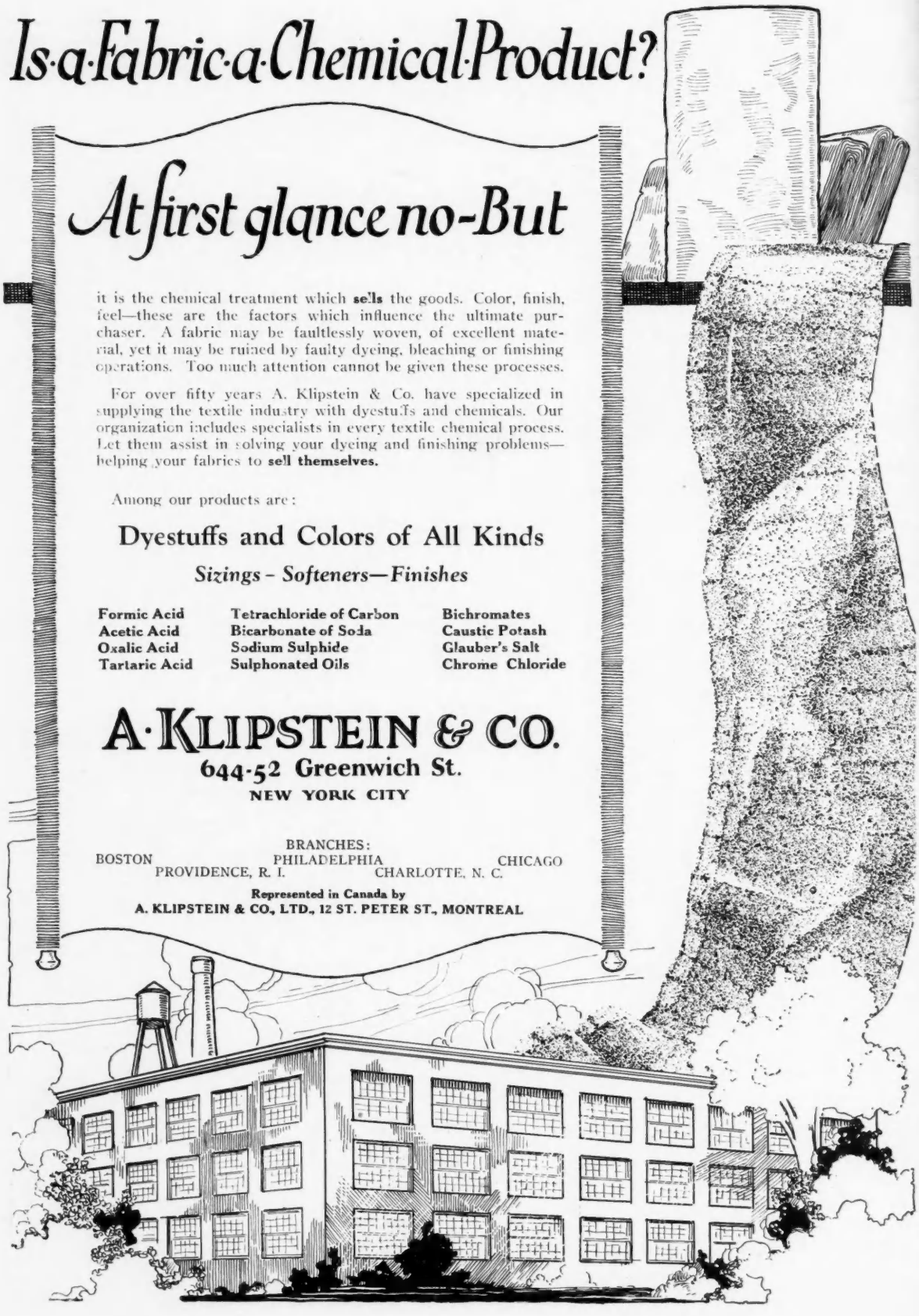
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